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Vibrational Spectra of 1,2,4,5-Tetracyanobenzene and 1,2,4,5-Tetracyanobenzen-d_2 Crystals

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Polarized IR and far-IR spectra of single crystals of 1,2,4,5-tetracyanobenzene and 1,2,4,5-tetracyanobenzene-d_2 were recorded. Polarized Raman spectra of these samples were also obtained at various geometries of the sample excitation and polarization. The results were analyzed under the assumption of the oriented gas model. The assignment of the fundamental frequencies was made with the aid of the isotope frequency shift and the spectral data of related compounds. The normal coordinate calculations were carried out with the modified Urey-Bradley force field and the valence force field for the in-plane and out-of-plane vibrations, respectively.

INTRODUCTION

Vibrational spectra of fully conjugated cyano-compounds such as tetracyanoethylene (TCNE),[1~6] 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 7,7,8,8-tetracyanoquinodimethane-d_4 (TCNQ-d_4)[7~10] have been studied in this laboratory and by other investigators. In the present work, we have dealt with vibrational spectra and normal coordinate analysis of 1,2,4,5-tetracyanobenzene (TCNB) and 1,2,4,5-tetracyanobenzene-d_2 (TCNB-d_2), which have been known as strong electron acceptors in charge-transfer complexes.

The interpretation of the complex spectra of these molecules should be based on the experimental results. In this point of view, detailed studies of IR spectra were made of single crystals of TCNB and TCNB-d_2 by the use of polarized radiations incident not only normally but also obliquely upon the plane of the crystal. Polarized far-IR spectra were also recorded for these samples. Polarization measurements of Raman spectra of the single crystals were carried out at various geometries of the sample excitation and polarization. The results obtained were analyzed on the basis of the assumption of the oriented gas model (the molecular symmetry D_{2h}), and the observed IR and Raman bands were confidently classified into the three IR-active and four Raman-active symmetry species, respectively.

The fundamental frequencies were assigned by referring to the isotope frequency

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shift and the spectral data of analogous molecules. The normal corrdinate calculations were carried out using the modified Urey-Bradley force field and the valence force field for the in-plane and out-of-plane vibrations, respectively. The agreement between the observed and calculated frequencies was satisfactory.

EXPERIMENTAL AND CRYSTAL STRUCTURE

A sample of TCNB was synthesized from pyromellitic acid according to Lawton and McRichie[11] and others.[12,13] That of TCNB-d_2 was synthesized by the same method from pyromellitic anhydride-d_2, which was obtained by dry distillation of mellitic acid-d_6 in the presence of sulfuric acid-d_2 and potassium bisulfate-d. Both the samples were recrystallized several times from acetic acid and from methyl ethyl ketone. Crystalline samples of TCNB and TCNB-d_2 thus obtained were colourless thin plates and melted at 269°C (reported m.p. 270–272°C[12]).

The crystal structure of TCNB has been determined by X-ray diffraction studies of Prout and Tickle[14] as a monoclinic system of space group $P2_1/a-C_{2h}^5$, with four molecules in a unit cell $a=13.79$ Å, $b=10.44$ Å, $c=6.51$ Å, and $\beta=112.0°$. The present X-ray diffraction studies for the TCNB and TCNB-d_2 crystals showed that the both crystals had the same structures as reported one,[14] and that the sample planes developed were the bc crystal plane, the c crystal axis being parallel to the direction of the crystal growth.

Polarized IR spectra of the single crystals of about 10×20 mm and of suitable thickness were recorded on a Perkin-Elmer model 521 spectrophotometer equipped with a wire grid polarizer of the silver bromide substrate. Polarized far-IR spectra between 400 and 30 cm^{-1} were obtained by a Hitachi model FIS-3 vacuum spectrophotometer equipped with a wire grid polarizer of the polyethylene substrate. Polarization measurements of Raman spectra were carried out for thick single crystals by the use of a Spex Ramalog spectrophotometer and a JEOL model SI spectrophotometer with the excitation line 632.8 nm of a HeNe gas laser.

Table I. Correlation Diagram and Selection Rules*

Molecular group $D_{2h}\equiv V_h$	Site group C_1	Factor group C_{2h}
8 a_g(R, p)		42 A_g(R, p)
7 b_{1g}(R, dp)		
2 b_{2g}(R, dp)		42 B_g(R, dp)
4 b_{3g}(R, dp)		
3 a_u(i.a.)		42 A_u(IR, T_b)
4 b_{1u}(IR, T_z†)		
7 b_{2u}(IR, T_y†)		42 B_u(IR, T_{ac})
7 b_{3u}(IR, T_x†)		

* R: Raman-active, IR: infrared-active, i.a.: inactive, p: polarized, dp; depolarized.
† For the molecular-fixed axes x, y, and z, see Fig. 6.

SELECTION RULES

The free molecules of TCNB and TCNB-d_2 have the $D_{2h} \equiv V_h$ symmetry. The selection rules for the free molecule and those for the molecules in the crystal are given in the correlation diagram of Table I. The vibrations belonging to the a_g, b_{1g}, b_{2u}, and b_{3u} species of the free molecule are the in-plane modes and those belonging to the remaining species are the out-of-plane modes. Table I shows that, irrespective of its intrinsic activity, each of forty-two normal vibrations of the free molecule splits in the crystal into two Raman-active modes (A_g and B_g) and two IR-active modes (A_u and B_u).

POLARIZED IR AND RAMAN SPECTRA

An attempt was first made of experimental classification of the IR bands into three species b_{1u}, b_{2u}, and b_{3u} of the free molecule under the assumption of the oriented gas model.

Figure 1 represents the polarized IR spectra of the TCNB and TCNB-d_2 crystals recorded on normal incidence of radiation upon the *bc* plane. Figure 2 shows the spectra of the TCNB and TCNB-d_2 crystals obtained by rotating the sample planes in turn by either of $+40°$ (the solid line) and $-40°$ (the broken line) about the *b* axis using the polarized radiation with electric vector parallel to the *ac* plane. Careful examination of Figs. 1 and 2 indicates that the absorption bands can be classified by their polarization properties into three groups:

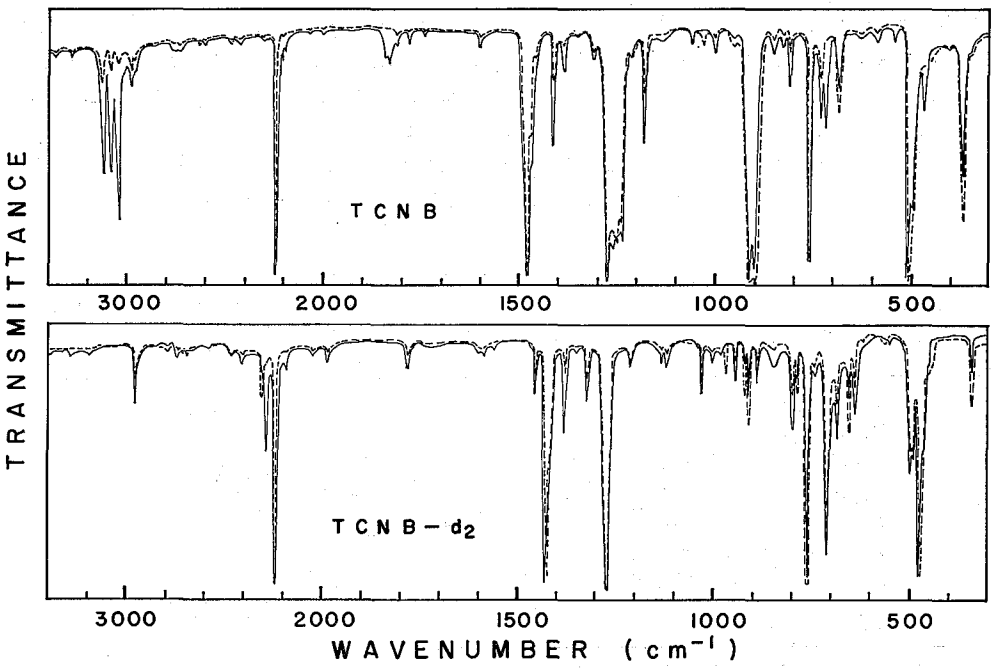

Fig. 1. Polarized IR spectra of the TCNB and TCNB-d_2 crystals.
——: electric vector parallel to the *c* axis.
– – –: electric vector parallel to the *b* axis.

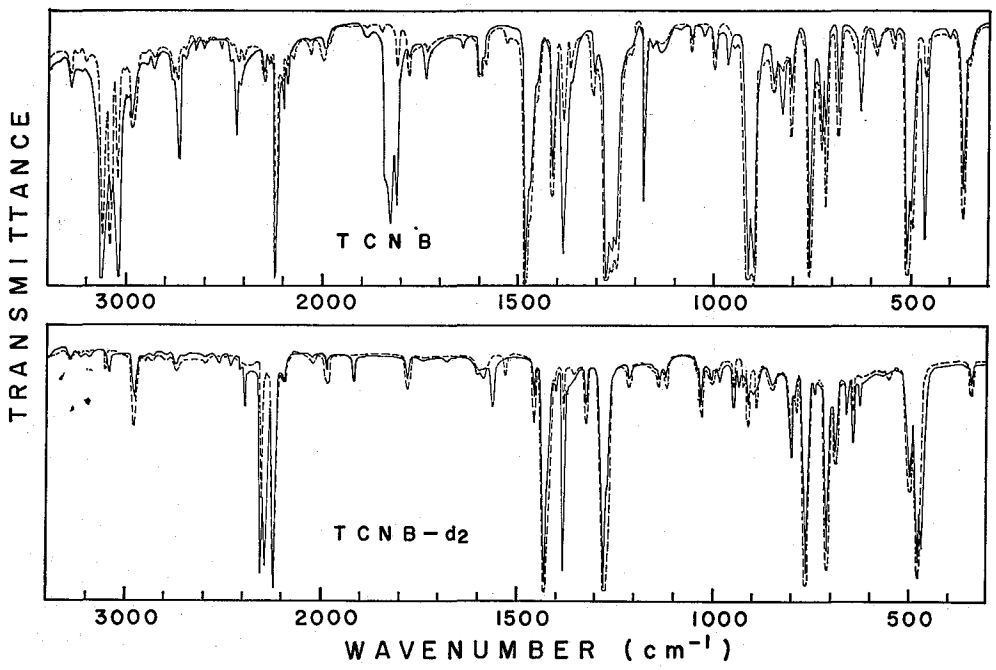

Fig. 2. IR spectra of the TCNB and TCNB-d_2 crystals obtained by rotating the crystal plane by $+40°$ (——) and $-40°$ (- - -) about the b axis using the polarized radiation with electric vector parallel to the ac plane.

I. A group of bands which give rise to the b-axis polarization in Fig. 1.
II. A group of bands which give rise to the c-axis polarization in Fig. 1. In Fig. 2, they largely increase their intensities, showing very stronger absorption for the solid line than for the broken line.
III. A group of bands which give rise to the c-axis polarization in Fig. 1, showing the stronger absorption for the broken line than for the solid line in Fig. 2.

Each group may correspond to one of three IR-active species of the molecular group D_{2h}. It is to be noted that the bands belonging to Groups II and III widely spread over the whole spectral region, while the bands belonging to Group I are restricted mainly in the lower frequency region. This fact suggests that Group I corresponds to the out-of-plane species b_{1u}.

The C-H stretching vibration of TCNB and the C-D stretching vibration of TCNB-d_2 (both belonging to the b_{2u} species) are expected to appear around 3100 and 2300 cm^{-1}, respectively, showing the same polarization property. In fact, three strong absorption bands are observed at 3119, 3087, and 3054 cm^{-1} in the TCNB spectra. The 3119 and 3054-cm^{-1} bands have the polarization property characteristic of Group II and the 3087-cm^{-1} band characteristic of Group III. In the TCNB–d_2 spectra, on the other hand, two absorption bands are observed at 2310 and 2292 cm^{-1}. The former has polarization property characteristic of Group I and the latter of Group II. The fact that the 3119- and 3054-cm^{-1} bands of TCNB and the 2292-cm^{-1} band of TCNB-d_2 have the same polarization property (characteristic of

Group II) suggests that these bands can be assigned to the C-H and C-D stretching vibrations belonging to the b_{2u} species. This means that Group II corresponds to the b_{2u} species. Since no other fundamental vibration is expected in this region, the two absorption bands at 3119 and 3054 cm^{-1} (belonging to the same species) in the TCNB spectra is likely to be due to the Fermi resonance between the C-H stretching vibration and a combination tone (see Table II). By the same reason, the 3087-cm^{-1} band (Group III) of TCNB and the 2310-cm^{-1} band (Group I) of TCNB-d_2 are ascribed to combination tones.

The correspondence of Group II to the b_{2u} species is further confirmed as follows: According to Kakiuti,[15] 1,2,4,5-tetrasubstituted benzenes are expected to have a moderately strong band around 1800 cm^{-1}, which is due to the combination tone (the b_{2u} species) between the C-H out-of-plane deformation vibrations. In fact, an IR band with the polarization properties characteristic of Group II is observed at 1827 cm^{-1} in the TCNB spectra. The corresponding band of TCNB-d_2 can be found at 1565 cm^{-1}, showing the same polarization property.

On referring to the spectral data of 1,2,4,5-tetrasubstituted benzenes and their deuterated derivatives,[16~18] the strong doublet pair at 918 and 910 cm^{-1} in the TCNB spectra and the band at 762 cm^{-1} in the TCNB-d_2 spectra are undoubtedly assinged to the C-H and C-D out-of-plane deformation vibrations (the b_{1u} species), respectively. The fact that all of these bands have polarization properties characteristic of Group I suggests that this group corresponds to the b_{1u} species, as expected above. The doublet pair at 918 and 910 cm^{-1} in the TCNB spectra may also due to the Fermi resonance between the C-H out-of-palne deformation vibration and some combination tone.

As a consequence of the above discussions, Group III may correspond to the b_{3u} species. The absorption band at 1485 cm^{-1} in the TCNB spectra and that at 1427 cm^{-1} in the TCNB-d_2 spectra have the typical polarization properties of this group.

In this manner, the IR bands observed can be classified into the three species without serious difficulties. This fact suggests that the assumption of the oriented gas model holds fairly well in the TCNB and TCNB-d_2 crystals. The factor group splitting of the intramolecular vibrations expected from Table I is observed only for a few bands such as the 507- and 504-cm^{-1} bands in the TCNB spectra.

Figure 3 represents polarized far-IR spectra of the TCNB and TCNB-d_2 crystals recorded on normal incidence of radiation upon the *bc* plane. The fact that the polarized spectra of the both crystals bear a close resembrance to each other in the region lower than 300 cm^{-1} suggests that these absorption bands consist of the intramolecular skeletal vibrations and the lattice vibrations.* The classification of the observed intramolecular bands to the respective species was made with the aid of the dichroism observed in Fig. 3 and the normal coordinate analysis mentioned later.

* According to the factor group analysis, there are twenty-one lattice vibrations of the structure, Γ (lattice) $=6A_g+6B_g+5A_u+5B_u$.

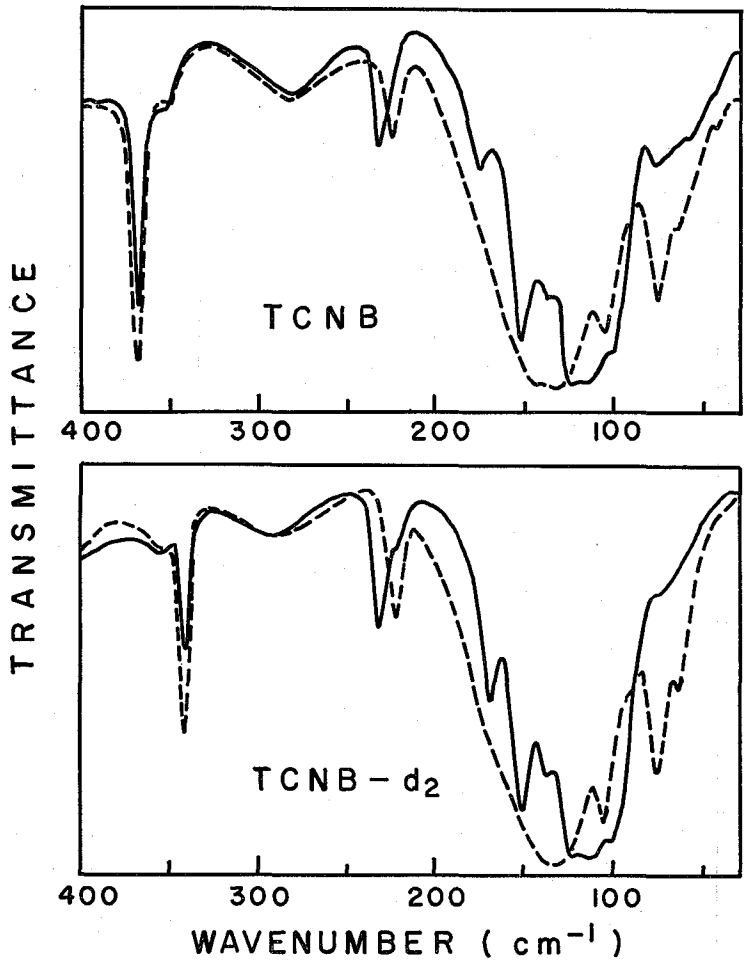

Fig. 3. Polarized far-IR spectra of the TCNB and TCNB-d_2 crystals.
——: electric vector parallel to the c axis.
– – –: electric vector parallel to the b axis.

Various polarized Raman spectra of the TCNB and TCNB-d_2 crystals are reproduced in Figs. 4 and 5, respectively, by the use of Porto's notation.[19] The a' axis refers to the axis normal to the bc plane. Pronounced effects of polarization can be seen in these figures. On the basis of the factor group analysis, the Raman bands observed in the $(a'a')$, (bb), (cc), and $(a'c)$ spectra can be classified into the A_g species and those observed in the $(a'b)$ and (bc) spectra into the B_g species.[20] Careful examination of Figs. 4 and 5, however, indicates that the Raman lines can be classified by their polarization properties into four groups:

I′. A group of lines which have the largest intensity in one of the $(a'a')$, (bb), and (cc) spectra.

II′. A group of lines which have the largest intensity in the $(a'c)$ spectrum.

III′. A group of lines which have the largest intensity in the $(a'b)$ spectrum.

IV′. A group of lines which have larger and nearly the same intensity in the $(a'b)$

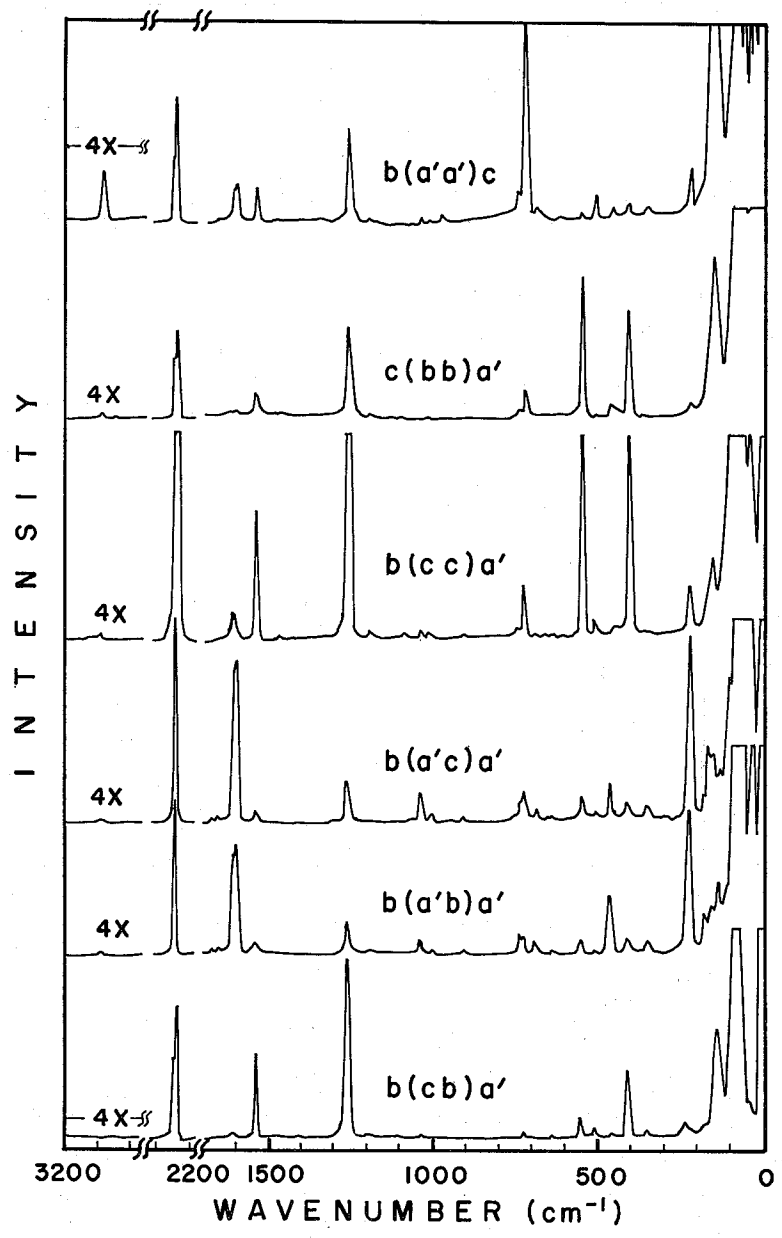

Fig. 4. Polarized Raman spectra of the TCNB crystal.

and $(a'c)$ spectra.

This is reasonable when the assumption of the oriented gas model holds well as in this case. Each group may correspond to one of four species a_g, b_{1g}, b_{2g}, and b_{3g} of the molecular group. The Raman lines belonging to Group I′ are undoubtedly classified into the a_g species. In fact, the 3087-cm^{-1} line of TCNB and the 2298-cm^{-1} line of TCNB-d_2 assignable to the C-H and C-D stretching vibrations of the a_g species

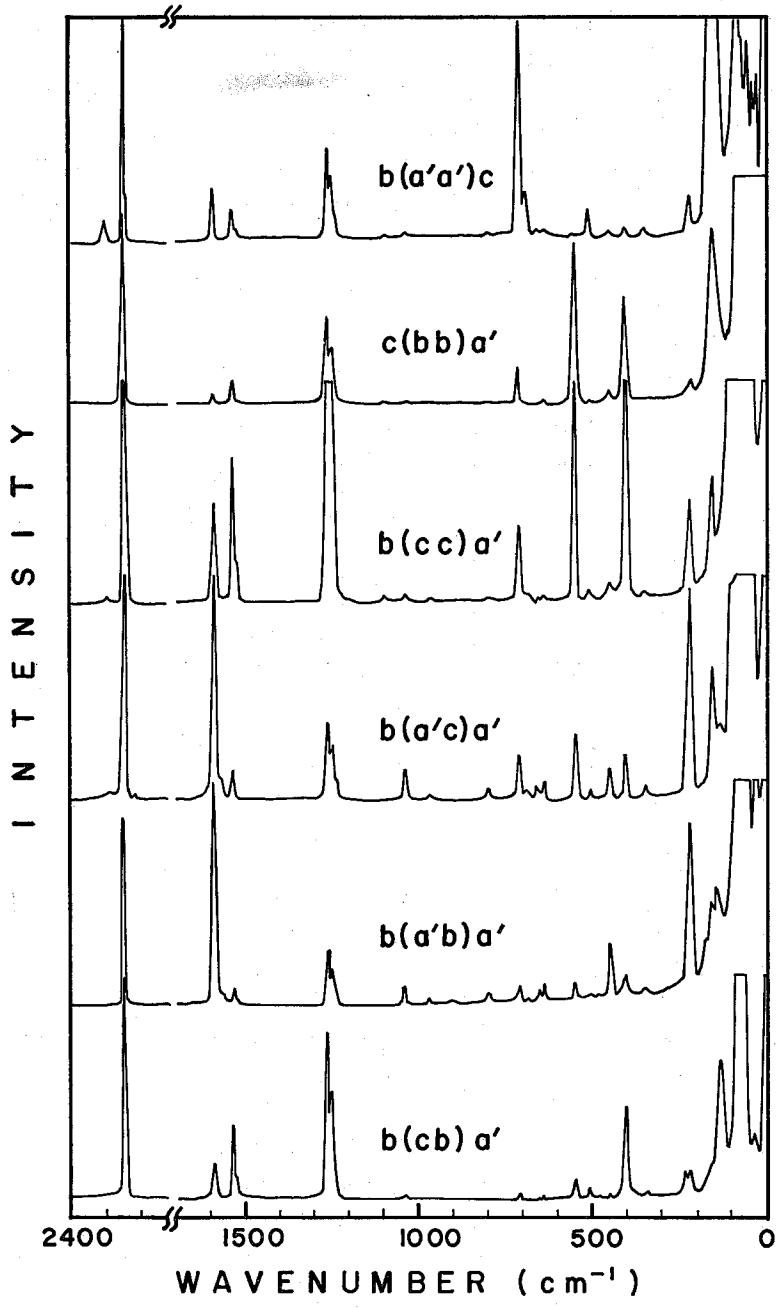

Fig. 5. Polarized Raman spectra of the TCNB-d_2 crystal.

appear only in the ($a'a'$) spectra. The 726-cm^{-1} line of TCNB and the 711-cm^{-1} line of TCNB-d_2 are also the strongest in the ($a'a'$) spectra among all the polarized spectra. On the other hand, the Raman lines of TCNB at 1541, 1256, 552, and 407 cm^{-1} and those of TCNB-d_2 at 1535, 1261, 1250, 552, and 405 cm^{-1} are the strongest in the (cc) spectra, and can also be classified into the a_g species. The

doublet pair at 1261 and 1250 cm^{-1} in the TCNB-d_2 spectra are due to the Fermi resonance between the fundamental vibration and a combination tone (see Table III).

By analogy with the spectral data of 1,2,4,5-tetrachlorobenzene[16~18] and with the aid of the normal coordinate analysis, the 1605-cm^{-1} line of TCNB and the 1590-cm^{-1} line of TCNB-d_2 are assigned to the ring stretching vibrations belonging to the b_{1g} species. Since these lines apparently have the same polarization properties

Table II. In-Plane Fundamental Vibrations of TCNB

Symmetry species		Obs. freq. (cm^{-1})	Calc. freq. (cm^{-1})	Dev.** (%)	P.E.D. (%)†
a_g	ν_1	3087	3097	0.3	C−H stretch (100)
	ν_2	2251	2251	0.0	C≡N stretch (90)
	ν_3	1541	1543	0.1	CCN−CCN (ring) stretch (54)
	ν_4	1256	1261	0.4	CCN−CH (ring) stretch (48), C−CN stretch (44)
	ν_5	726	730	0.5	C−CH−C (ring) bend (36), CCN−CCN (ring) stretch (30)
	ν_6	552	557	0.9	C≡N bend (54), C−CN bend (41)
	ν_7	407	406	−0.2	C−CH−C (ring) bend (34), C−CN stretch (30)
	ν_8	143	135	−5.3	C−CN bend (53), C≡N bend (45)
b_{1g}	ν_9	2247	2249	0.1	C≡N stretch (90)
	ν_{10}	1605	1609	0.2	CCN−CH (ring) stretch (61)
	ν_{11}	1262	1266	0.3	C−H bend (79)
	ν_{12}	1041	1048	0.6	C−CN stretch (64)
	ν_{13}	707	701	−0.8	C−CN bend (81)
	ν_{14}	350	349	−0.2	C−C−CH (ring) bend (74)
	ν_{15}	224	225	0.4	C≡N bend (85)
b_{2u}	ν_{16}	3087*	3098	0.3	C−H stretch (100)
	ν_{17}	2250	2249	0.0	C≡N stretch (90)
	ν_{18}	1388	1391	0.2	CCN−CH (ring) stretch (57)
	ν_{19}	1218	1226	0.6	C−CH−C (ring) bend (31), C−C−CH (ring) bend (30)
	ν_{20}	628	626	−0.3	Ring deform‡
	ν_{21}	466	466	0.0	C≡N bend (36)
	ν_{22}	152	152	0.0	C−CN bend (46), C≡N bend (42)
b_{3u}	ν_{23}	2250	2250	0.0	C≡N stretch (90)
	ν_{24}	1485	1488	0.2	C−H bend (47)
	ν_{25}	1278	1276	−0.2	CCN−CCN (ring) stretch (52), CCN−CH (ring) stretch (37)
	ν_{26}	1181	1164	−1.4	C−H bend (48)
	ν_{27}	762	763	0.1	C−CN stretch (56)
	ν_{28}	498	499	0.2	C−CN bend (56), C≡N bend (39)
	ν_{29}	128	125	−2.3	C≡N bend (62), C−CN bend (37)

* Mean value of the 3119- and 3054-cm^{-1} bands (see text).
** Dev.$=100[\nu(\text{calc})-\nu(\text{obs})]/\nu(\text{obs})$.
† Only contributions greater than 30 % are included.
‡ Contribution greater than 30 % are not present.

Table III. In-Plane Fundamental Vibrations of TCNB-d_2*

Symmetry species		Obs. freq. (cm^{-1})	Calc. freq. (cm^{-1})	Dev. (%)	P.E.D. (%)
a_g	ν_1'	2298	2286	−0.5	C−D stretch (97)
	ν_2'	2251	2250	0.0	C≡N stretch (90)
	ν_3'	1535	1534	0.0	CCN−CCN (ring) stretch (55)
	ν_4'	1256**	1254	−0.2	CCN−CD (ring) stretch (49), C−CN stretch (45)
	ν_5'	711	708	−0.4	C−CD−C (ring) bend (36), CCN−CCN (ring) stretch (30)
	ν_6'	552	557	0.9	C≡N bend (55), C−CN bend (40)
	ν_7'	405	405	0.0	C−CD−C (ring) bend (35), C−CN stretch (30)
	ν_8'	143	135	−5.3	C−CN bend (52), C≡N bend (45)
b_{1g}	ν_9'	2247	2249	0.1	C≡N stretch (90)
	ν_{10}'	1590	1589	−0.1	CCN−CD (ring) stretch (68)
	ν_{11}'	1040	1048	0.8	C−CN stretch (64)
	ν_{12}'	970	977	0.7	C−D bend (78)
	ν_{13}'	655	661	0.9	C−CN bend (69)
	ν_{14}'	346	349	0.9	C−C−CD (ring) bend (74)
	ν_{15}'	220	222	1.0	C≡N bend (84)
b_{2u}	ν_{16}'	2292	2288	−0.2	C−D stretch (95)
	ν_{17}'	2250	2249	−0.0	C≡N stretch (90)
	ν_{18}'	1379	1382	0.2	CCN−CD (ring) stretch (53)
	ν_{19}'	1211	1207	−0.4	C−CD−C (ring) bend (32), C−CN stretch (30)
	ν_{20}'	620	618	−0.3	Ring deform†
	ν_{21}'	466	466	0.0	C≡N bend (36)
	ν_{22}'	151	152	0.5	C−CN bend (46), C≡N bend (42)
b_{3u}	ν_{23}'	2250	2250	0.0	C≡N stretch (90)
	ν_{24}'	1427	1417	−0.7	CCN−CD (ring) stretch (30)
	ν_{25}'	1272	1275	0.3	CCN−CCN (ring) stretch (50), CCN−CD (ring) stretch (41)
	ν_{26}'	945	933	−1.3	C−D bend (59), C−CN stretch (36)
	ν_{27}'	710	712	0.3	C−CN stretch (34)
	ν_{28}'	497	499	0.4	C−CN bend (56), C≡N bend (39)
	ν_{29}'	127	125	−1.6	C≡N bend (62), C−CN bend (37)

* Symbols as in Table II.
** Mean value of the 1261- and 1250-cm^{-1} bands (see text).
† Contributions greater than 30 % are not present.

characteristic of Group II′, the lines belonging to this group can be classified into the b_{1g} species. As a consequence of the same kind of examinations, Group III′ and IV′ are classified into the b_{2g} and b_{3g} species, respectively.

ASSIGNMENT OF FUNDAMENTAL VIBRATIONS

In order to make assignment of the observed frequencies to the fundamental vibrations, the following examinations were carried out besides the discussions in

Table IV. Out-of-plane Fundamental Vibrations of TCNB and TCNB-d_2*

Symmetry species			Obs. freq. (cm^{-1})	Calc. freq. (cm^{-1})	Dev. (%)	P.E.D. (%)
TCNB	b_{2g}	ν_{30}	463	461	−0.4	C≡N bend (75)
		ν_{31}	178	180	1.0	C−CN bend (75)
	b_{3g}	ν_{32}	909	888	−2.3	C−H bend (79)
		ν_{33}	736	728	−1.1	C−CN bend (46), Ring torsion (42)
		ν_{34}	368	367	−0.2	C≡N bend (85)
		ν_{35}	77	79	2.8	C−CN bend (57)
	a_u	ν_{36}	—	751	—	C−CN bend (47), Ring torsion (42)
		ν_{37}	—	356	—	C≡N bend (85)
		ν_{38}	—	41	—	C−CN bend (52), Ring torsion (44)
	b_{1u}	ν_{39}	914**	905	−1.0	C−H bend (85)
		ν_{40}	506†	522	3.2	Ring torsion (39), C≡N bend (32)
		ν_{41}	369	361	−2.2	C≡N bend (63), Ring torsion (32)
		ν_{42}	64	61	−4.5	C−CN bend (66)
TCNB-d_2	b_{2g}	ν_{30}'	453	461	1.8	C≡N bend (75)
		ν_{31}'	178	180	1.0	C−CN bend (75)
	b_{3g}	ν_{32}'	801	812	1.3	C−D bend (44), Ring torsion (32)
		ν_{33}'	640	639	−0.2	C−D bend (49)
		ν_{34}'	354	357	0.7	C≡N bend (82)
		ν_{35}'	74	73	−1.5	C−CN bend (56)
	a_u	ν_{36}'	—	751	—	C−CN bend (47), Ring torsion (42)
		ν_{37}'	—	356	—	C≡N bend (85)
		ν_{38}'	—	41	—	C−CN bend (52), Ring torsion (44)
	b_{1u}	ν_{39}'	762	792	3.9	C−D bend (70)
		ν_{40}'	476	480	0.9	C≡N bend (57)
		ν_{41}'	341	325	−4.6	C≡N bend (45), Ring torsion (41)
		ν_{42}'	64	60	−6.4	C−CN bend (65)

* Symbols as in Table II.
** Mean value of 918- and 910-cm^{-1} bands (see text).
† Mean value of 507- and 504-cm^{-1} bands (see text).

the previous section: (a) Comparisons of the spectral data with those of the analogous molecules, such as TCNE,[1~6] TCNQ,[7~10] and 1,2,4,5-tetrachlorobenzene.[16~18] (b) The application of the product rule to the TCNB and TCNB-d_2 fundamental vibrations. (c) The normal coordinate analysis for the in-plane and out-of-plane vibrations of TCNB and TCNB-d_2.

The observed frequencies thus determined as the in-plane fundamental vibrations of TCNB and TCNB-d_2 are listed in Tables II and III, respectively. Those assigned to the out-of-plane fundamental vibrations are also listed in Table IV. In these tables, the mean values of frequencies are cited whenever the band splitting occurs owing to the Fermi resonance or the factor group splitting. It is to be noted that the fundamental vibrations belonging to the a_u species of the molecular group can be

Table V. Application of the Product Rule of Fundamental Vibrations of TCNB and TCNB-d_2

	a_g	b_{1g}	b_{2g}	b_{3g}	a_u	b_{1u}	b_{2u}	b_{3u}
Theoretical	0.71	0.71	1	0.72	1	0.71	0.71	0.71
Experimental	0.72	0.68	0.98	0.71	—	0.72	0.72	0.71

detected neither in the IR spectra nor in the Raman spectra of the TCNB and TCNB–d_2 crystals.

Table V shows the results of the application of the product rule to the TCNB and TCNB-d_2 fundamental vibrations. A good agreement was found between the theoretical and the experimental values of $\Pi[\nu_k(\text{TCNB-}d_2)/\nu_k(\text{TCNB})]$ for all but the a_u species just mentioned.

NORMAL COORDINATE ANALYSIS

The GF matrix method[21] was used for the normal coordinate analysis of the in-plane and out-of-plane fundamental vibrations. The numerical calculations were carried out with the aid of a Facom 230–60 computer of the Data Processing Center of Kyoto University by using a program coded by Machida. The internal coordinates are given in Figs. 6a and 6b. The equilibrium bond lengths adopted are the mean values of those obtained for the TCNB molecule[14]: $L_1^0=L_2^0=1.03$ Å, $R_1^0=R_3^0=R_4^0=R_6^0=1.398$ Å, $R_2^0=R_5^0=1.405$ Å, $r_1^0=\cdots=r_4^0=1.446$ Å, and $l_1^0=\cdots=l_4^0=1.140$ Å. For the bond angles, $\theta_1^0=\cdots=\theta_{18}^0=120°$ and $\theta_{19}^0=\cdots=\theta_{22}^0=180°$ were assumed for the sake of simplicity.

As the potential function for the in-plane vibrations, the modified Urey-Bradley force field (UBFF) defined by

$$
\begin{aligned}
2V(\text{UBFF}) &= 2V(\text{basic UBFF}) \\
&+C[\text{CH}\cdots\text{CH(ring)}](\Delta q_1)^2+2C'[\text{CH}\cdots\text{CH(ring)}]q_1^0(\Delta q_1) \\
&+\sum_{i=2}^{3}\{C[\text{CCN}\cdots\text{CCN(ring)}](\Delta q_i)^2+2C'[\text{CCN}\cdots\text{CCN(ring)}]q_i^0(\Delta q_i)\} \\
&+\sum_{j=4}^{5}\{\text{C}[\text{CN}\cdots\text{CN(side)}](\Delta q_j)^2+2C'[\text{CN}\cdots\text{CN(side)}]q_j^0(\Delta q_j)\} \\
&+\sum_{k=6}^{9}\{\text{C}[\text{CN}\cdots\text{H(side)}](\Delta q_k)^2+2C'[\text{CN}\cdots\text{H(side)}]q_k^0(\Delta q_k)\} \\
&+\rho\{\sum^{6}(\Delta R_m)(\Delta R_{m+1})-\sum^{6}(\Delta R_m)(\Delta R_{m+2})+\sum^{3}(\Delta R_m)(\Delta R_{m+3})\} \\
&+\alpha\sum_{n=1}^{4}(\Delta r_n)(\Delta l_n)+\beta[(\Delta\theta_{19})(\Delta\theta_{22})+(\Delta\theta_{20})(\Delta\theta_{21})] \\
&+\gamma[(\Delta R_2)\{(\Delta\theta_{11}-\Delta\theta_{12})+(\Delta\theta_{14}-\Delta\theta_{13})\}+(\Delta R_5)\{(\Delta\theta_{15}-\Delta\theta_{16}) \\
&+(\Delta\theta_{18}-\Delta\theta_{17})\}]
\end{aligned}
$$

was used. The basic UBFF potential V (basic UBFF) consists of the five bond-stretching force constant, K(C-H), K(C≡N), K[CCN-CCN(ring)], K[CCN-CH (ring)], and K(C-CN), six angle-bending force constants, H[C-CH-C(ring)], H [C-C-CH(ring)], H[CN-C-CH(side)], H[CN-C-C(side)], H(C-C-H), and H(C-C≡N),

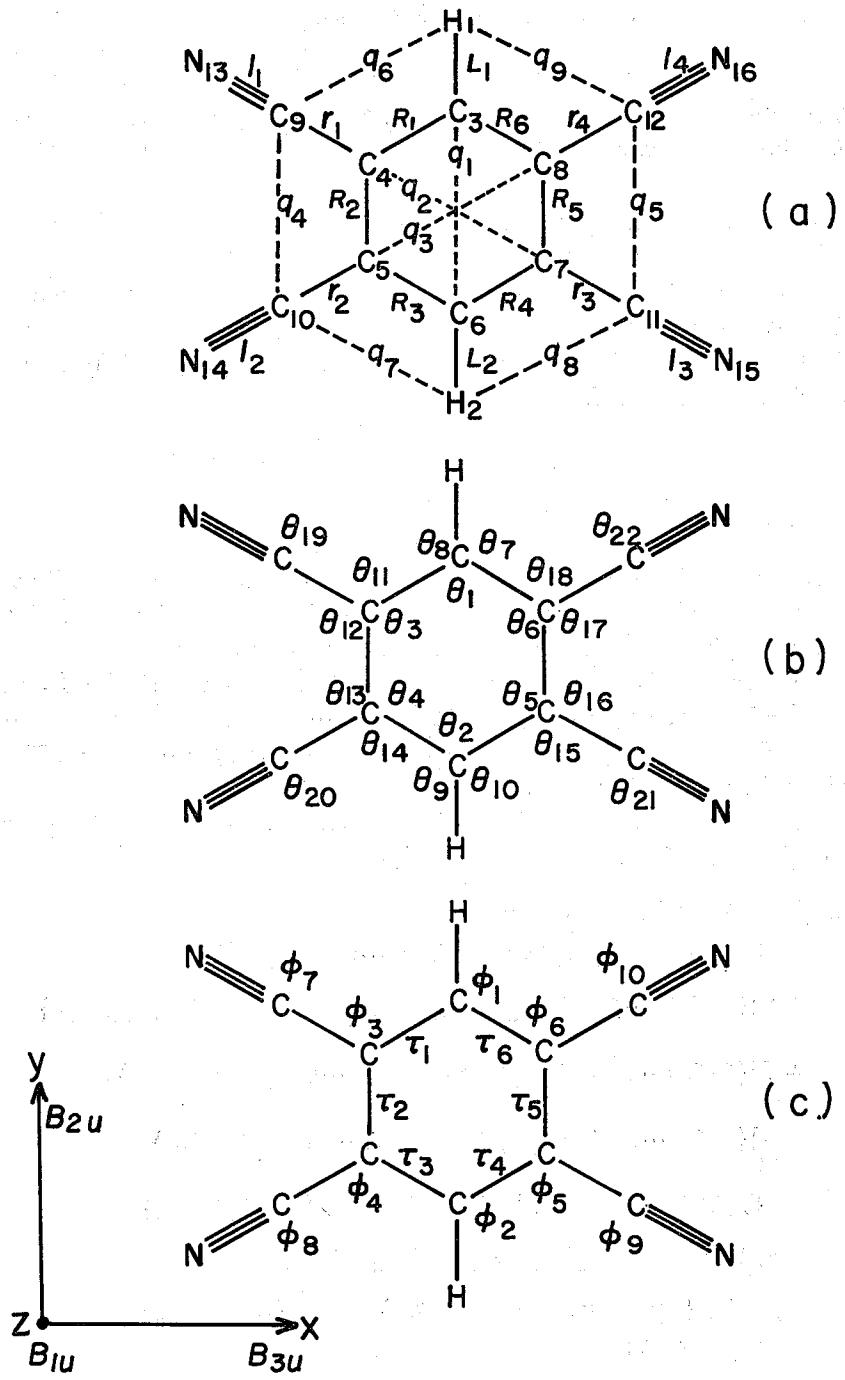

Fig. 6. Internal coordinates of TCNB.

and five *gem* non-bonded repulsion force constants, F[C-CH-C(ring)], F[C-C-CH (ring)], F[CN-C-CH(side)], F[CN-C-C(side)], and F(C-C-H). The symbols, for

example, K[CCN-CCN(ring)], H[C-CH-C(ring)], and F[CN-C-CH(side)] represent the stretching force constant for the bond R_2 or R_5 in the benzene ring, the bending force constant for the angle θ_1 or θ_2 in the benzene ring, and the repulsion force constant between the *gem* non-bonded atoms $C_3\cdots C_9$, $C_6\cdots C_{10}$, $C_6\cdots C_{11}$, or $C_3\cdots C_{12}$, respectively. The force constants C's and ρ refer to the *cis* non-bonded repulsions and the Kekulé interaction, [22,23] respectively. The force constant α, β, and γ are the coefficients of cross terms introduced to have a better agreement between the observed and calculated frequencies.

In the initial calculation, the values of the force constants were trasferred from TCNE,[1] TCNQ,[8] and 1,2,4,5-tetrachlorobenzene.[24] After some refinements of the values by the trial-and-error method using the Jacobian matrix, repetitions of the calculation with several sets of the force constants were carried out by the least-squares method. The converged set of the force constants thus obtained and their dispersions are shown in Table VI. The calculated frequencies for the TCNB and TCNB-d_2 molecules with this set of the force constants are given in Tables II and

Table VI. In-Plane Force Constanst* (mdyne/Å)

		Force const.	Dispersion
1	K(C−H)	4.92	0.08
2	K(C≡N)	18.51	0.13
3	K[CCN−CCN (ring)]	4.94	0.12
4	K[CCN−CH(ring)]	5.05	—‡
5	K(C−CN)	4.58	0.18
6	H[C−CH−C (ring)]	0.47	0.06
7	H[C−C−CH (ring)]	0.15	0.06
8	H[CN−C−CH (ring)]	0.29	0.05
9	H[CN−C−C (side)]	0.25	0.05
10	H(C−C−H)	0.24	0.02
11	H(C−C≡N)	0.19	0.00
12	F [C−CH−C (ring)]	0.40	0.09
13	F [C−C−CH (ring)]	0.57	0.17
14	F [CN−C−CH (side)]	0.37	0.10
15	F [CN−C−C (side)]	0.71	0.10
16	F (C−C−H)	0.27	0.06
17	C [CH···CH (ring)]	−0.09	0.07
18	C [CCN···CCN (ring)]	0.11	0.03
19	C [CN···CN (side)]	0.15	0.02
20	C [CN···H (side)]	0.05	0.02
21	ρ	0.30	0.01
22	α	0.90	0.00
23	β**	0.08	0.00
24	γ†	−0.14	0.00

* The relations $F'=-0.1F$ and $C'=-0.1C$ were assumed.
** mdyne·Å/rad².
† mdyne/rad.
‡ Fixed.

III, respectively. The agreement between the calculated and observed values is satisfactory. The last columns of Tables II and III represent the potential energy distribution.

The force constants given in Table VI are reasonable in magnitude. The larger value 4.58 mdyne/Å of K(C-CN) is consistent with the corresponding values of TCNE (4.80 mdyne/Å)[1] and TCNQ (4.89 mdyne/Å).[8] The result that the force constants K[CCN-CCN(ring)], K[CCN-CH(ring)], and K(C-CN) have nearly the same values suggests that resonance takes place almost completely over the whole molecule of TCNB.

As the potential function for the out-of-plane vibrations, the valence force field (VFF) expressed by

$$2V(\mathrm{VFF}) = Y(\mathrm{C\text{-}C}) \sum_{i=1}^{6} (\Delta\tau_i)^2 + \Pi(\mathrm{C\text{-}H}) \sum_{j=1}^{2} (\Delta\phi_j)^2 + \Pi(\mathrm{C\text{-}CN}) \sum_{k=3}^{6} (\Delta\phi_k)^2 + \Pi(\mathrm{C{\equiv}N}) \sum_{l=7}^{10} (\Delta\phi_l)^2 + \sigma\sum^{6}(\Delta\tau_m)(\Delta\tau_{m+1}) + \delta[(\Delta\phi_1)(\Delta\phi_3+\Delta\phi_6) + (\Delta\phi_2)(\Delta\phi_4+\Delta\phi_5)]$$

was used according to Scherer.[25] The internal coordinates are given in Fig. 6C. The diagonal terms consist of the torsional force constant Y(C-C) of the C-C bond in the benzene ring, and three angle-bending force constants Π(C-H), Π(C-CN), and Π(C≡N). Besides those, the interaction constants σ between the adjacent torsional coordinates in the benzene ring and δ between the C-H angle-bending coordinate and the adjacent C-CN angle-bending coordinate were used.

The starting values of the force constants were transferred from chlorinated benzene.[25] The converged set of the force constants obtained by the least-squares method is shown in Table VII, together with their dispersion values. The calculated

Table VII. Out-of-Plane Force Constants (mdyne·Å/rad²)

	Force const.	Dispersion
1 Y(C−C)	0.34	0.03
2 Π(C−H)	0.36	0.01
3 Π(C−CN)	0.22	0.01
4 Π(C≡N)	0.32	0.01
5 σ	0.12	0.01
6 δ	0.11	0.01

frequencies for the TCNB and TCNB-d_2 molecules with these force constants are compared with the observed values in Table IV, showing the satisfactory agreement. The potential energy distributions are also listed in this table. The atomic displacements of the fundamental vibrations of TCNB and TCNB-d_2 in terms of the Cartesian displacement coordinates have been calculated and reported elsewhere.[26]

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